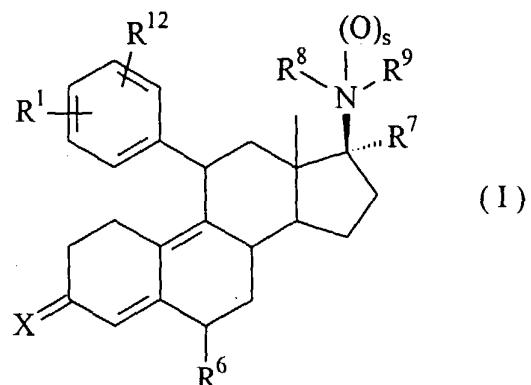


WHAT IS CLAIMED AS NEW AND DESIRED TO BE SECURED BY LETTERS
PATENT OF THE UNITED STATES IS:

1. A hormonal or antihormonal steroid compound of structure I,

5



10

wherein

R¹ is (R² R³ N(O)_r)-, where r is 0 or 1 and R² and R³ are each independently H, C₁₋₆

alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl or C₂₋₆ alkynyl, any of which may be optionally substituted;

or

R¹ is Y-CH₂-N^{(O)q}-CH₂-, where q is 0 or 1, Y is -(CH₂)_m- where m is an integer of

15 0 to 5, or Y is -(CH₂)_n-Z-(CH₂)_p- where n is an integer of 0 to 2, p is an integer of

0 to 2, and Z is a heteroatom (optionally substituted) and where any of the CH₂ groups may

be optionally substituted; or

R¹ is N-imidazolyl-, N-pyrrolyl-, H, halo-, HO-, CF₃SO₂O-, C₁₋₆ alkyl-O-, C₁₋₆ alkyl-S-,

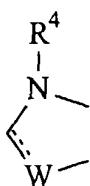
C₁₋₆ alkyl-S(O)-, C₁₋₆ alkyl-S(O₂)-, C₁₋₆ alkyl-CO-, C₁₋₆ alkyl-CH(OH)-, NC-, HCC-, C₆H₅CC-,

20 2'-furyl, 3'-furyl, 2'-thiophenyl, 3'-thiophenyl, 2'-pyridyl, 3'-pyridyl, 4'-pyridyl, 2'-thiazolyl,

2'-N-methylimidazolyl, 5'-pyrimidinyl, C₆H₅-, H₂C=CH-, C₁₋₆ alkyl, or MeC(=CH₂)-;

R¹² is H or halo; or

R¹ and R¹² combine to form a ring



5 where W is CH₂, CH, NH, N, O, or S, and R⁴ is H or C₁₋₆ alkyl;

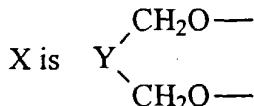
X is O or NOR⁵, where R⁵ is H or C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl,

C₆₋₁₂ aryl, or heteroaryl, any of which may be optionally substituted; or

X is (H, H), (H, OH), (H, OSi(C₁₋₆ alkyl)₃), or (H, OCOR⁵), where R⁵ is C₁₋₆ alkyl,

C₃₋₈ cycloalkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl,

10 heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally substituted; or

X is  where Y is -(CH₂)_m- where m is an integer of 0 to 3, or Y is -(CH₂)_n-Z-(CH₂)_p- where n is an integer of 0 to 2, p is an integer of 0 to 2 and Z is a

15 heteroatom (optionally substituted) or Z is a carbon atom substituted with one or two C₁₋₆ alkyl groups;

R⁶ is H, C₁₋₆ alkyl or halogen;

R⁷ is H, C₁₋₆ alkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl,

aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of

20 which may be optionally substituted, CN, COOR¹⁰ or CONHR¹⁰, where R¹⁰ is H, C₁₋₁₈ alkyl, C₂₋₁₈ alkenyl, C₂₋₁₈ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally substituted;

s is 0 or 1;

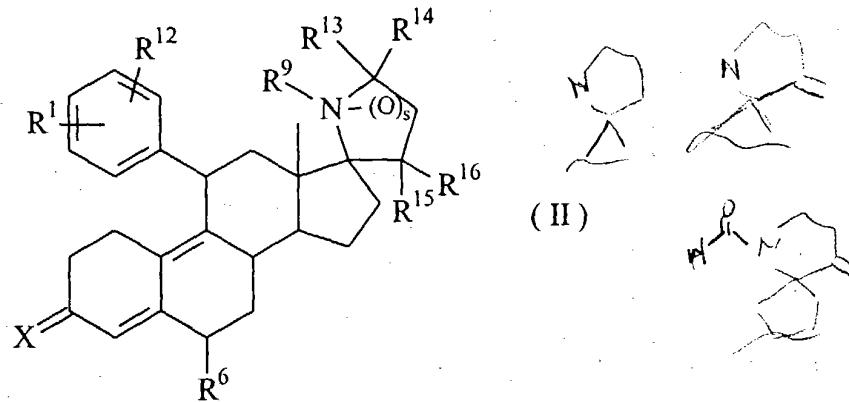
R^8 and R^9 are each independently H, C_{1-6} alkyl, C_{2-6} alkenyl or C_{2-6} alkynyl, $R^{10}CO$, OR^{11} , any of which may be optionally substituted,

where R¹⁰ is H, C₁₋₁₈ alkyl, C₂₋₁₈ alkenyl, C₂₋₁₈ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl,
5 aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl any of
which may be optionally substituted, and

where R^{11} is H, C_{1-6} alkyl, $Si(C_{1-6} \text{ alkyl})_3$, 2'-tetrahydropyranyl or $R^{10}CO$ where R^{10} is as defined above; and

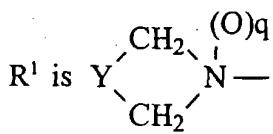
wherein when s is 0, R⁸ may also be O⁻ and R⁹ is =CH₂ or =C(H, C₁₋₆), =C(H, aryl) or =C(C₁₋₆)₂ and the nitrogen attached to the 17-position is positively charged; and pharmaceutically acceptable salts thereof.

2. A hormonal or antihormonal steroid compound of structure II,



wherein

20 R¹ is (R² R³ N(O)_r)-, where r is 0 or 1 and R² and R³ are each independently H, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl or C₂₋₆ alkynyl, any of which may be optionally substituted; or



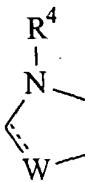
R¹ is $\text{Y} \text{---} \text{CH}_2 \text{---} \text{N} \text{---} \text{(O)}\text{q}$, where q is 0 or 1, Y is $-(\text{CH}_2)_m-$ where m is an integer of 0 to 5, or Y is $-(\text{CH}_2)_n\text{---}Z\text{---}(\text{CH}_2)_p-$ where n is an integer of 0 to 2, p is an integer of 0 to 2, and Z is a heteroatom (optionally substituted) and where any of the CH₂ groups may

5 be optionally substituted; or

R¹ is N-imidazolyl-, N-pyrrolyl-, halo-, HO-, CF₃SO₂O-, C₁₋₆ alkyl-O-, C₁₋₆ alkyl-S-, C₁₋₆ alkyl-S(O)-, C₁₋₆ alkyl-S(O₂)-, C₁₋₆ alkyl-CO-, C₁₋₆ alkyl-CH(OH)-, NC-, HCC-, C₆H₅CC-, 2'-furyl, 3'-furyl, 2'-thiophenyl, 3'-thiophenyl, 2'-pyridyl, 3'-pyridyl, 4'-pyridyl, 2'-thiazolyl, 2'-N-methylimidazolyl, 5'-pyrimidinyl, C₆H₅-, H₂C=CH-, C₁₋₆ alkyl, or MeC(=CH₂)-;

10 R¹² is H or halo; or

R¹ and R¹² combine to form a ring



where W is CH₂, CH, NH, N, O, or S, and R⁴ is H or C₁₋₆ alkyl;

15 X is O or NOR⁵, where R⁵ is H or C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₆₋₁₂ aryl, or heteroaryl, any of which may be optionally substituted; or

X is (H, H), (H, OH), (H, OSi(C₁₋₆ alkyl)₃), or (H, OCOR⁵), where R⁵ is C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally

20 substituted; or

X is $\text{Y} \text{---} \text{CH}_2\text{O} \text{---}$, where Y is $-(\text{CH}_2)_m-$ where m is an integer of 0 to 3, or Y is $-(\text{CH}_2)_n\text{---}Z\text{---}(\text{CH}_2)_p-$ where n is an integer of 0 to 2, p is an integer of 0 to 2 and Z is a heteroatom (optionally substituted) or Z is a carbon atom substituted with one or two C₁₋₆

alkyl groups;

R⁶ is H, C₁₋₆ alkyl or halogen;

s is 0 or 1;

R⁹ is H, C₁₋₆ alkyl, C₂₋₆ alkenyl or C₂₋₆ alkynyl, R¹⁰CO, OR¹¹, any of which may be

5 optionally substituted,

where R¹⁰ is H, C₁₋₁₈ alkyl, C₂₋₁₈ alkenyl, C₂₋₁₈ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl any of which may be optionally substituted, and

where R¹¹ is H, C₁₋₆ alkyl, Si(C₁₋₆ alkyl)₃, 2'-tetrahydropyranyl or R¹⁰CO where R¹⁰ is

10 as defined above;

R¹³ and R¹⁴ are each independently H, C₁₋₁₈ alkyl, C₂₋₁₈ alkenyl, C₂₋₁₈ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl, aralkenyl or aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally substituted; or R¹³ R¹⁴ is O, and

15 R¹⁵ and R¹⁶ are each H or combine to form a group =CH₂, optionally substituted, and pharmaceutically acceptable salts thereof.

3. The steroid having structure I of claim 1 wherein

R¹-Ph is 4-aminophenyl, 4-(N-methylamino)phenyl, 4-(N,N-dimethylamino)phenyl, 4-(N-piperidino)phenyl, 4-(N-pyrrolidino)phenyl, 4-(N-morpholino)phenyl, 1-methylindol-5-yl or 1-m or ethyl-2,3-dihydroindol-5-yl or R¹-Ph is the N-oxide of 4-(N,N-dimethyl)phenyl, 4-(N-piperidino)phenyl, 4-(N-pyrrolidino)phenyl, 4-(N-morpholino)phenyl;

X is O, NOH, or NOCH₃;

R⁶ is H, CH₃, F or Cl;

R^7 is H, methyl, ethynyl, 1-propynyl, 3-propynyl, 3-hydroxypropyl, 3-hydroxy-1-propenyl (*E*- or *Z*-), 3,3,3-trifluoropropyn-1-yl, 3-hydroxypropyn-1-yl, $(CH_2)_2COOCH_3$, $(CH_2)_2COOC_2H_5$, $(CH_2)_2COCH_3$, $CC-C_6H_5$, $CH_2C_6H_5$, CN, or $COOCH_3$;

R^8 is H, CH_3 , or $CH_2C_6H_5$; and

R⁹ is H, OH, OCH₃, CHO, CH₃CO, C₆H₅CO or C₆H₅CH₂CO.

4. The steroid of Claim 2, wherein

R¹-Ph is 4-aminophenyl, 4-(N-methylamino)phenyl, 4-(N,N-dimethylamino)phenyl, 4-(N-piperidino)phenyl, 4-(N-pyrrolidino)phenyl, 4-(N-morpholino)phenyl, 1-methylindol-5-yl or 1-methyl-2,3-dihydroindol-5-yl;

X is O, NOH, or NOCH₃;

R^6 is H, CH_3 , F or Cl;

R⁹ is H, OH, CHO, CH₃CO, C₆H₅CO or C₆H₅CH₂CO;

R^{13} and R^{14} are O, (H, H), (H, CH_3) or (CH_3 , CH_3); and

R^{15} and R^{16} are (H, H) or $R^{15} R^{16}$ is ($=CH_2$).

5. The steroid of Claim 1 selected from the group consisting of:

(N-piperidino)phenyl)-17 α -(1-propynyl)estra-4,9-dien-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-17 β -(N-formamido)-17 α -(1-propynyl)estra-4,9-dien-3-one and its N-oxide, 17 β -(N-formamido)-11 β -(4-(N-piperidino)phenyl)-17 α -(1-propynyl)estra-4,9-dien-3-one and its N-oxide, 11 β -(4-(N,N-dimethylamino)phenyl)-17 β -(N-hydroxylamino)-17 α -(3-hydroxypropyl)-estra-4,9-dien-3-one, 11 β -(4-(N-piperidino)phenyl)-17 β -(N-hydroxylamino)-17 α -(3-hydroxypropyl)-estra-4,9-dien-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-17 β -(N-hydroxy-N-methylamino)-17 α -(3-hydroxypropyl)estra-4,9-dien-3-one, 11 β -(4-(N-piperidino)phenyl)-17 β -(N-hydroxy-N-methylamino)-17 α -(3-hydroxypropyl)estra-4,9-dien-3-one, 17 β -amino-11 β -(4-(N,N-dimethylamino)phenyl)-17 α -(3-hydroxypropyl)estra-4,9-dien-3-one, 17 β -amino-17 α -(3-hydroxypropyl)-11 β -(4-(N-piperidino)phenyl)estra-4,9-dien-3-one, 17 β -(N-acetamido)-11 β -(4-(N,N-dimethylamino)phenyl)-17 α -(3-hydroxypropyl)estra-4,9-dien-3-one, 17 β -(N-acetamido)-17 α -(3-hydroxypropyl)-11 β -(4-(N-piperidino)phenyl)estra-4,9-dien-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-17 β -(N-formamido)-17 α -(3-hydroxypropyl)estra-4,9-dien-3-one and 17 β -(N-formamido)-17 α -(3-hydroxypropyl)-11 β -(4-(N-piperidino)phenyl)estra-4,9-dien-3-one and 17 β -(N-formamido)-17 α -(3-formyloxy-1-propyl)estra-4,9-dien-3-one and 17 β -(N-formamido)-17 α -(3-formyloxy-1-propyl)-11 β -(4-(N-piperidino)phenyl)estra-4,9-dien-3-one.

6. The steroid of Claim 2, selected from the group consisting of

20 11 β -(4-(N,N-dimethylamino)phenyl)-1'-hydroxy-5'-methyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N-piperidino)phenyl)-1'-hydroxy-5'-methyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-1'-hydroxy-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N-piperidino)phenyl)-1'-hydroxy-spiro[estra-4,9-

dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-5'-methyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N-piperidino)phenyl)-5'-methyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N-piperidino)phenyl)-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-5'-oxo-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N-piperidino)phenyl)-5'-oxo-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one, 11 β -(4-(N,N-dimethylamino)phenyl)-1'-formyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one and 11 β -(4-(N-piperidino)phenyl)-1'-formyl-spiro[estra-4,9-dien-17 β ,2'-pyrrolidine]-3-one.

10 7. A method of therapeutically treating the activity of progesterone comprising administering a therapeutically effective amount of the compound of Claim 1, to a patient in need thereof for a therapeutic purpose.

8. The method of claim 7, wherein said therapeutic purpose is the treatment of endometriosis or uterine fibroids.

15 9. The method of claim 7, wherein said therapeutic purpose is cervical ripening preparatory to labor and delivery of offspring.

10. The method of claim 7, wherein said therapeutic purpose is the control or regulation of fertility.

11. The method of claim 7, wherein said therapeutic purpose is the treatment of tumors or cancers.

12. The method of claim 7, wherein said therapeutic purpose is hormone replacement therapy.

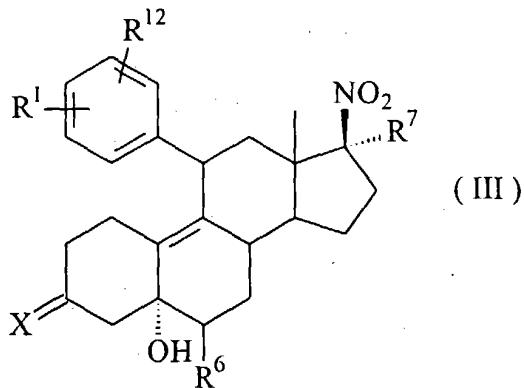
13. A method of therapeutically treating the activity of progesterone comprising

administering a therapeutically effective amount of the compound of Claim 2, to a patient in need thereof for a therapeutic purpose.

14. A method of preparing the compound of Claim 1, comprising:

i) treating a compound of structure (III) by reduction of the nitro group, followed by

5 hydrolysis of X and elimination of the hydroxyl group



wherein

R¹ is (R² R³ N(O)_r)-, where r is 0 or 1 and R² and R³ are each independently H, C₁₋₆

alkyl, C₃₋₈ cycloalkyl, C₂₋₆ alkenyl or C₂₋₆ alkynyl, any of which may be optionally substituted;

or

15 R¹ is Y- $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} \text{---} \text{O}^q \end{array}$, where q is 0 or 1, Y is -(CH₂)_m- where m is an integer of

0 to 5, or Y is -(CH₂)_n-Z-(CH₂)_p- where n is an integer of 0 to 2, p is an integer of

0 to 2, and Z is a heteroatom (optionally substituted) and where any of the CH₂ groups may

be optionally substituted; or

R¹ is N-imidazolyl- N-pyrrolyl-, H, halo-, HO-, CF₃SO₂O-, C₁₋₆ alkyl-O-, C₁₋₆ alkyl-S-

20 , C₁₋₆ alkyl-S(O)-, C₁₋₆ alkyl-S(O₂)-, C₁₋₆ alkyl-CO-, C₁₋₆ alkyl-CH(OH)-, NC-, HCC-, C₆H₅CC-

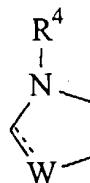
, 2'-furyl, 3'-furyl, 2'-thiophenyl, 3'-thiophenyl, 2'-pyridyl, 3'-pyridyl, 4'-pyridyl, 2'-

thiazolyl, 2'-N-methylimidazolyl, 5'-pyrimidinyl, C₆H₅- , H₂C=CH-, C₁₋₆ alkyl, or

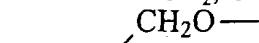
MeC(=CH₂)-;

R¹² is H or halo; or

R¹ and R¹² combine to form a ring



5 where W is CH₂, CH, NH, N, O, or S, and R⁴ is H or C₁₋₆ alkyl;



X is Y, where Y is -(CH₂)_m- where m is an integer of 0 to 3, or Y is -

(CH₂)_n-Z-(CH₂)_p- where n is an integer of 0 to 2, p is an integer of 0 to 2 and Z is a

heteroatom (optionally substituted) or Z is a carbon atom substituted with one or two C₁₋₆

alkyl groups;

10 R⁶ is H, C₁₋₆ alkyl or halogen;

R⁷ is H, C₁₋₆ alkyl, C₂₋₆ alkenyl, C₂₋₆ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally substituted, CN, COOR¹⁰ or CONHR¹⁰, where R¹⁰ is H, C₁₋₁₈ alkyl, C₂₋₁₈ alkenyl, C₂₋₁₈ alkynyl, C₃₋₈ cycloalkyl, C₆₋₁₂ aryl, aralkyl, aralkenyl, aralkynyl, heteroaryl, heteroaralkyl, heteroaralkenyl or heteroaralkynyl, any of which may be optionally substituted.

15 15. A method of therapeutically treating the activity of progesterone comprising administering a therapeutically effective amount of the compound of Claim 2, to a patient in need thereof for a therapeutic purpose.

16. The method of Claim 7, further comprising administering one or more pharmacologically active compounds.

20 17. The method of Claim 15, further comprising administering one or more pharmacologically active compounds.